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REACTIONS OF AROMATIC NITROCOMPOUNDS.
I. PHOTOCHEMISTRY

Oscar Sandus, et al

Picatinny Arsenal
Dover, New Jersey

December 1972

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I. PHOTOCHEMISTRY

OSCAR SANDUS
NORMAN SLAGG

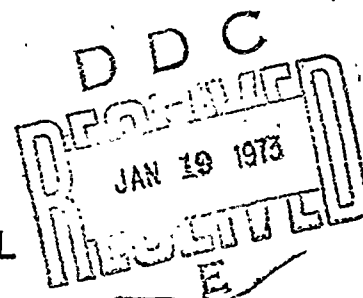
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<p>The flash photolysis and continuous photolysis at 2537A ($\pi \rightarrow \pi^*$ transitions) of aromatic nitrocompounds in solution were performed.</p> <p>Flash photolysis revealed intermediates for o-nitrotoluene and its nitor derivatives. The spectrum and mean lifetime of the intermediate for flash TNT were determined. The maximum absorption of the TNT intermediate occurred in the 470 nm region and the mean lifetime was 1.5 ± 0.3 msec. This intermediate is probably not directly related to product formation.</p> <p>The continuous photolysis experiments reveals that all the aromatic nitrocompounds have disappearance quantum yields of the order 10^{-3}. These low values for the quantum yields imply that the most important reaction occurring is the deactivation to the ground state of the original molecule. The presence or absence of oxygen does not appear to be of significance.</p> <p>Product analyses suggest that aromatic nitrosocompounds and nitrophenols are main products. However, the observed products do not conform in a simple manner to the constraints of the isosbestic points observed in all photolyses. It appears that other products are present, some of which may have low extinction coefficients in the spectral range studied. The latter may be necessary to accommodate the isosbestic points.</p>			

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	Aromatic nitrocompounds Flash photolysis Continuous photolysis Solution photochemistry Disappearance quantum yields Isosbestic points Explosives Intermediates Photochromic (or phototropic) molecules Nitro- and nitrosobenzene Procedures and apparatus Spectral data						

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Explosives Division
Feltman Research Laboratory
Picatinny Arsenal
Dover, New Jersey

I

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ABSTRACT

The flash photolysis and continuous photolysis at 2537⁰Å ($\pi \rightarrow \pi^*$ transitions) of aromatic nitrocompounds in solution were performed.

Flash photolysis revealed intermediates for o-nitrotoluene and its nitro derivatives. The spectrum and mean lifetime of the intermediate for flashed TNT were determined. The maximum absorption of the TNT intermediate occurred in the 470 nm region and the mean lifetime was 1.5 ± 0.3 msec. This intermediate is probably not directly related to product formation.

The continuous photolysis experiments reveals that all the aromatic nitrocompounds have disappearance quantum yields of the order 10^{-3} . These low values for the quantum yields imply that the most important reaction occurring is the deactivation to the ground state of the original molecule. The presence or absence of oxygen does not appear to be of significance.

Product analyses suggest that aromatic nitrosocompounds and nitrophenols are main products. However, the observed products do not conform in a simple manner to the constraints of the isosbestic points observed in all photolyses. It appears that other products are present, some of which may have low extinction coefficients in the spectral range studied. The latter may be necessary to accommodate the isosbestic points.

INTRODUCTION

A search of the literature reveals that very little is known about the decomposition processes, bond energies, and thermodynamic properties of aromatic nitrocompounds. TNT and TNB (trinitrobenzene) are explosives of military interest that fall into this class of compounds. With the idea of eventually being able to gain some control of the explosive processes, a study of aromatic nitrocompounds was initiated. Since a molecule must decompose via its ground state or one of its excited states, the initial phase of the study was concerned with the photochemistry of these compounds using both continuous photolysis at 2537Å and flash photolysis. Photochemical studies can reveal the nature of excited states, sites of attack, and bond energies. Since the vapor pressure of many of the compounds is low, solution photochemistry appeared most suitable for elucidating primary processes.

Photochemical Considerations

The number of states to which a molecule in the ground state can go as a result of energy absorption is finite. By using radiation, the behavior of these upper states can be studied.

Figure 1 represents the energy levels of a typical organic molecule containing a π -electron system. S_0 is the ground electronic state, which is a singlet; S_1 denotes the first excited singlet state; and T_1 and T_2 represent the first and second triplet states, respectively. Each of the states shows some vibrational energy levels. Some of the processes that occur when there is interaction between the molecule and an electromagnetic field, whose energy is in the visible or ultraviolet region of the spectrum, are as follows: In process (1), the molecule absorbs a photon and is raised to the excited single state (S_1). From S_1 the molecule can undergo one of several processes. The most rapid process, which occurs in solution ($\sim 10^{-12} - 10^{-13}$ sec) and is caused by collisions, is a radiationless loss of excess vibrational energy (process (2)). The molecule is now in the lowest

vibrational level of the first excited singlet state whose lifetime is $\sim 10^{-8}$ seconds. There are three processes by which a molecule can leave the excited singlet state. Process (3) depicts internal conversion, which is a radiationless deactivation to the ground state. Process (4) shows a transition to the ground state where the molecule emits radiation called fluorescence. Process (5) illustrates intersystem crossing where the molecule crosses from the first excited singlet state to the first triplet state. By internal conversion, the molecule reaches the lowest vibrational level to T_1 . The molecule reaches the lowest vibrational level of T_1 . The molecule can return to the ground state S_0 by radiationless intersystem crossing (process (6)). Since the selection rules forbidding radiative transitions between states of different multiplicities are not strict, the lifetimes are usually $\sim 10^{-3}$ second or longer, although shorter lifetimes have been observed. When no collisional deactivation occurs during this lifetime, deactivation to the ground state can take place (process (7)) radiatively by phosphorescence, a long-lived luminescence. The advent of flash photolysis has made possible observation of triplet-triplet absorption due to the usually long lifetime of the triplet state (process (8)).

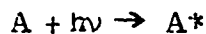
In addition to the processes described, a molecule may enter into reactions from either an excited singlet or triplet state. Other excited configurations are possible when the molecule consists of complex energy levels.

In the work presented in this report, two methods were used to study the aromatic nitrocompounds. These are: continuous photolysis and flash photolysis.

Continuous photolysis involves irradiating a solution with light of one wavelength for a specific time and determining the number of molecules reacted and the number of quanta absorbed. The quantum yield or quantum efficiency for the disappearance of the nitrocompound can be calculated from the definition:

$$\Phi = \frac{\text{No. of molecules chemically reacted}}{\text{No. of quanta absorbed}}$$

The quantum yield is a good indicator as to the possible mechanisms that are prevalent in a reaction. Suppose molecule A is irradiated and is raised to an excited state, designated A*:



A* can behave in a number of ways to give various quantum yields, as depicted in Table 1.

TABLE 1

The relationship between mechanism and disappearance quantum yield

<u>Mechanism</u>	<u>Φ (Quantum Yield for Disappearance)</u>
(1) $A^* \rightarrow A + h\nu$	0
(2) $A^* \rightarrow B$ or $A^* + C \rightarrow D + E$	1
(3) $A^* + A \rightarrow B$	2
(4) $\begin{cases} A^* \rightarrow B \\ A^* + A \rightarrow C \end{cases}$	1 - 2
(5) $\begin{cases} A^* \rightarrow B \\ A^* \rightarrow A + h\nu \text{ or } A^* + M \rightarrow A + M \end{cases}$	0 - 1
(6) $\begin{aligned} &A^* \rightarrow R_1 + R_2 \\ &\left. \begin{aligned} &R_1 + A \rightarrow B + R_3 \\ &R_3 + A \rightarrow C + R_1 \end{aligned} \right\} \text{(Propagation)} \\ &\left. \begin{aligned} &R_3 + A \rightarrow C + R_1 \\ &R_1 + R_3 + (M) \rightarrow D + (M) \end{aligned} \right\} \begin{aligned} &\text{(Repeated)} \\ &\text{Termination} \end{aligned} \end{aligned}$	$\gg 1$

B, C, D, and E represent stable product molecules; R_1 , R_2 , and R_3 represent free radicals, and M represents a third body.

If A^* returns to the ground state through fluorescence, as mechanism (1) shows, or by any of the other ways indicated previously, the quantum yield is zero. Now, if A^* is rearranged to a stable molecule or reacts with a molecule other than A and stable products are formed as depicted in mechanism (2), then the quantum yield is one. On the other hand, if A^* reacts with another molecule to A to form a stable product or products, then the quantum yield equals 2, as mechanism (3) shows. When there are competing reactions, the quantum yield will not be a whole number. In the case of mechanism (4), A^* disappears in two reactions so that the quantum yield is between 1 and 2 and will depend upon the relative importance of each of the reactions. The quantum yield can be less than one, if the competing steps indicated in mechanism (5) occur. In the final case of mechanism (6), A^* decomposes into two radicals, R_1 and R_2 . R_1 reacts with A to produce a third radical, which in turn reacts with A to produce R_1 again. These chain propagation steps are repeated a great many times. This chain propagation may be stopped before exhaustion of A by a chain termination step where radicals can be deactivated by the presence of a third body, if required. It is generally believed that chain reactions are responsible for detonation. For example, the reaction between H_2 and Cl_2 leads to a quantum yield of 10^6 - 10^7 .

Photochromic (or phototropic) molecules have been studied for a long time. As with other stable molecules, these molecules exist in stable electronic configurations that give rise to their characteristic absorption spectra. However, when a photochromic substance is irradiated, usually with ultraviolet light, the molecules absorb the energy and are excited to an unstable configuration whose absorption spectrum is in the visible region, so that color is produced. The original unirradiated substance was either colorless or of a different color; hence the term photochromism. The color persists in a steady state condition as long as the substance is irradiated. However, when the irradiation is removed, the molecules return to their original stable electronic state. The mechanism for this involves very efficient pathways for internal conversion. Charge transfer is another mechanism that can lead to photochromism, but is mainly important for inorganic substances.

Review of Past Photochemical Studies

Several photochemical studies have been performed. They were mainly concerned with the 3600 Å region. The major studies are listed below.

TABLE 2

Review of Major Photochemical Studies

<u>Study</u>	<u>Conditions</u>	<u>Results</u>	<u>Conclusions</u>
Schultz and Ganguly 1925 (Ref 1)	Pulverized TNT in sunlight	Surface becomes colored	
Leighton and Lucy, 1934 (Ref 2)	Various wavelengths between 2654 and 4040 Å were utilized. o-Nitrobenzaldehyde; 2, 4-dinitrobenzaldehyde; and 2, 4, 6-trinitrobenzaldehyde were studied as solids in and solutions of acetone and ligroin	For o-nitrobenzaldehyde, quantum yield was independent of wavelength, oxygen, and state. Product was o-nitrosobenzoic acid.	Tautomeric quinoximes formed through unstable intermediate. In acetone, a stable intermediate formed. Intramolecular process.
Shelegova, 1939 (Ref 3)	Nitrobenzene vapor with various light sources	2900-2160 Å region: products are: phenol and NO ₂ . 2160-1850 Å: products are phenol and polynitrobenzenes	No evidence to support products postulated.
Hastings and Matsen, 1948 (Ref 4)	Nitrobenzene vapor irradiated by mercury arcs.	Main products were nitrosobenzene and p-nitrophenol	Absorption leads to release of O atom from NO ₂ group which inserts in parent molecule.
Gray, Bonomo, and Denner, 1962 (Ref 5)	Same as those by Schultz and Ganguly	Could not repeat work of Schultz and Ganguly (Ref 1)	No explanations
Margerum et al, 1962 (Ref 6)	Solutions of aromatic nitro-compounds in 95% alcohol. Photolyzed by an unfiltered 400 watt Hg lamp.	No compound found to be phototropic which did not have a nitrogroup ortho to a benzyl hydrogen	Intramolecular process that involves an H-atom transfer
Wettermark, 1962, 1963 (Ref 7, 8, 9)	Studied photolysis of o-nitrotoluene and dinitrotoluene. Flash photolyzed in water and alcohol.	Transients observed. Absorption spectra a function of pH	Intramolecular H-atom transfer.

<u>Study</u>	<u>Conditions</u>	<u>Results</u>	<u>Conclusions</u>
Tench and Copper (Ref 10)	Photolyzed o-nitrobenzaldehyde, nitrobenzene, and nitrobenzoic acid with light $>3500\text{\AA}$	ESR measurements revealed the presence of radicals for o-nitrobenzaldehyde (in solutions and powder). No radicals were observed with nitrobenzene and nitrobenzoic acid.	Photoradical occurs as a side reaction, is not the intermediate in the conversion of the nitro to the nitrosocompound.
Morrison and Migdalof, 1965 (Ref 11)	o-Nitrotoluene and o-nitrotoluene irradiated with Pyrex-filtered Hg lamp. D_2O and p-dioxane as solvents.	C-D bonds formed with o-nitrotoluene. No C-D formation for p-nitrotoluene.	H atom abstracted from solvent by intramolecular process.
Ward, 1963 Brown and Williams, 1966 (Ref 12a and b)	Studied nitrobenzene with radiation $>3300\text{\AA}$. Tetrahydrofuran (THF) as solvent. Degassed solutions. Effects of low temperatures were also studied.	ESR signal, attributed to the $C_6H_5N(O_2)H$ radical, obtained with THF as the solvent. No ESR signal was obtained when perfluoronaphthalene was added.	The triplet state of nitrobenzene is an intermediate.
Hurley and Testa, 1966 (Ref 13)	Nitrobenzene in isopropyl alcohol degassed and in air. Hg lamp at 3660\AA .	Products in the absence of air are acetone and phenylhydroxylamine (PHA). In air, PHA is oxidized to nitrosobenzene which couples with PHA to form azoxybenzene.	Triplet molecule abstracts H atoms from solvent. No effect with benzene as the solvent.
Hurley and Testa, 1967 (Ref 14)	Nitrobenzene in isopropyl alcohol-water mixtures containing HCl. Hg lamp at 3660\AA .	Quantum yields depend on pH and isopropyl alcohol content, but are independent of O_2 with acid present.	Quantum yield consists of two parts: H abstraction by the triplet, and protonation of the triplet

<u>Study</u>	<u>Conditions</u>	<u>Results</u>	<u>Conclusions</u>
Strom and Weistein, 1967 (Ref 15)	Used an unfiltered 200 watt Hg lamp. Degassed solutions of nitrocumene and o-nitrotoluene.	o-Nitrocumene radicals. For o-nitrotoluene yield was much less. Radicals were stable for days and could also be formed in the presence of O ₂ . No radicals with corresponding parasubstitute compounds.	The reaction proceeds via an intramolecular step.
Baltrop and Bunce, 1968 (Ref 16)	Various wavelengths, solvents, and nitrocompounds.	For $\lambda < 2900\text{\AA}$, aniline is the main product. For $> 2900\text{\AA}$, bimolecular species, such as azobenzene, are the main products. O ₂ had little effect on aniline production, so experiments performed in presence of O ₂ . For nitrobenzene in isopropyl alcohol, no azoxybenzene produced as with Hurley and Testa (Ref 13).	Excited state abstracts H atoms. Suggests nitrobenzene triplet is π, π^* state and nitrosobenzene is unobserved intermediate.
Hashimoto, Sunamoto, Fujii, and Kano, 1968 (Ref 17)	130-watt Hg lamp was used to irradiate isopropyl alcohol -HCl - nitrocompound solutions. Effect of O ₂ studied.	In the absence of HCl, nitrobenzene produces phenylhydroxylamine. When HCl is present, nitrobenzene produces aniline and other products.	Explanations of mechanism not given.
Weller and Hamilton, 1970 (Ref 18)	Irradiated solutions of nitrobenzene and alkanes with a 450-watt Hg lamp. Different glass filters used.	Good yields of alcohols and carbonyl compounds observed.	The oxidation involves an H-atom abstraction by nitrobenzene.
Ayscough, Sealy, and Woods, 1971 (Ref 19)	Irradiated nitroso- and nitrobenzene in isopropyl alcohol and other solvents. The incident wavelength was greater than 3000Å. Performed ESR studies on solutions.	Found stable radical $\text{C}_6\text{H}_5\dot{\text{N}}\text{OH}$	Participation of triplet state not involved with nitroso-compounds, and not firmly established with nitrocompounds.

The preceding summary illustrates the complexity of the kinetics through the contradictory results obtained by different workers. It is seen that Gray, et al, could not repeat the work of Schultz and Ganguly. Baltrop and Bunce found aniline under conditions similar to those of other workers who did not report it.

One complicating factor in the photolysis of aromatic nitro-compounds in the past was the fact that some products have higher extinction coefficients than the parent molecule. For example, at 313 nm the values of ϵ for nitro- and nitrosobenzene are about 288 and 2300, respectively. Thus, for this wavelength region, any nitrosobenzene formed will itself be photolyzed. A similar situation exists for nitroso- and nitrotoluene. One may therefore be able to partially explain some of the variations in results of photolyses in the 3100-3600Å region. Relative intensities of the wavelength components of the incident radiation and variations in the extent of photolysis of products contribute to the poor reproducibility of previous studies. These problems are expected to be less severe at 2537Å. At 2537Å the ϵ for nitro- and nitrosobenzene are 8810 and 2600, respectively, and for ortho-nitro- and orthonitrosotoluene the values are 5790 and 1790, respectively. Thus, products of this type formed in the photolysis at 2537Å are less likely to be further photolyzed and the interpretation of results should be easier.

EXPERIMENTAL PROCEDURES

Materials

The TNT (Eastman Kodak Company) was purified by the method described by Gey, Dalbey, and Dolah (Ref 20).

o-Nitrotoluene (Eastman Kodak Company) was fractionally recrystallized in a dry-ice bath and vacuum distilled. The middle third fraction was retained.

The middle third fraction of nitrobenzene (Fisher Scientific Company) was obtained by vacuum distillation.

o-Nitrosotoluene was prepared according to the method of Lutz and Lytton (Ref 21).

The other nitrocompounds used in the experiments, all of which were obtained from Eastman Kodak Company, were checked in solution with the Beckman DK-2 spectrophotometer in the visible and ultraviolet, and some were checked in a gas chromatograph as well.

The gas chromatograph employed a 9-foot column of 10% DC-25-X-30295 absorbed on 80-90 mesh Anakron ABS support to separate the nitrocompounds. A flame ionization detector was used and helium was the carrier gas. The temperature-time program operated between 100° and 225°C. No significant impurities were evident and the compounds were used as received.

Certified isopropyl alcohol (99 mol %) and spectranalyzed n-heptane and cyclohexane (Fisher Scientific Company) were used without further purification.

Flash Photolysis Apparatus

Figure 2 schematically depicts the flash photolysis apparatus. The spectral lamp used initially was a Sylvania R4340 flash lamp through which was discharged a 105 μ f capacitor charged to 2.5 KV. The mean lifetime ($\frac{1}{e}$) of the light pulse was approximately 350 μ sec.

The photolysis flash lamps were two Xenon Corporation FP-10-100A linear flash lamps connected in series and a 20 μ f capacitor charged to 10 KV was discharged across them. This gave an input energy of 1000 joules and a mean lifetime of about 35 μ sec for the light pulse. The delay between flashings of the lamps was obtained with an Electronic Aids time delay generator.

The quartz solution cell between the flash lamps was about 11.5 inches long having 1-inch-in-diameter optical windows at both ends. Two tubes were fused to the cell near the ends to allow for filling. An aluminum reflector partially enclosed the cell. The light passing lengthwise through the cell from the spectral flash lamp was monitored in the visible with a small Bausch and Lomb High Intensity Grating Monochromator with slits adjusted for a

nominal bandwidth slightly less than 2 nm, an RCA 1P28 photo-multiplier tube having a 10 K Ω resistor as a load to a Tektronix 585A oscilloscope and a Polaroid camera.

An experiment was performed by flashing the spectral flash lamp first and then the photolysis flash lamps 100 μ sec later, which is about at the peak intensity of the spectral flash lamp. By comparing oscilloscope traces for the spectral flash alone with those obtained in the experiments with both spectral and photolytic lamps at various wavelengths, the absorption spectrum and lifetime of an intermediate can be determined.

Although the spectra of the intermediates were determined in this manner, the lifetime could not be determined since they were longer than the lifetime of the spectral lamp. Therefore, a continuous light source, Oriel Optics Corporation 200-watt Xe-Hg Universal Arc Lamp, was used in place of the Sylvania flash lamp. Since this source was much lower in intensity than the photolysis flash lamps, it was necessary to monitor only the strong Hg lines and to interpose two slits between the diaphragm and the monochromator in order to increase the ratio of the signal of the spectral lamp to the signal of the scattered light from the photolysis flash lamps reaching the monochromator.

To minimize the effects of heat radiated from the Xe-Hg lamp on the solution, a Corning CS 1-58 infrared-absorbing, visible-transmitting filter was employed between the lamp and the cell. The temperature of the experiments was 25 - 30°C.

Some of the solutions were deaerated in the solution cell by flowing nitrogen through them for one hour. A flask containing some of the pure solvent was put between the cell and the nitrogen supply. Samples removed near the end of the nitrogen flushing indicated that no change in concentration occurs when such samples are investigated with the spectrophotometer.

The Polaroid records for only the first few flashes were used to obtain the intermediate spectrum and lifetime. This was done because products having absorption in the same region as the intermediate were formed, progressively increasing the complications of the records.

For product analysis, the solutions were usually flashed ten times each in order to obtain sufficient product concentrations. Differential analyses were performed in the Beckman DK-2 spectrophotometer using an unflashed solution as reference in most cases. The concentrations of the solutions were 10^{-4}M .

Continuous Photolysis

In continuous photolysis, a 1-cm Beckman cell containing 3 ml of a 10^{-5}M solution of the nitrocompound in n-heptane, isopropyl alcohol, or cyclohexane for TNT was placed in front of a low pressure mercury quartz pencil lamp (Spectronics Corporation). The predominant radiation was 2537\AA . A Corning CS9-54 filter was used to eliminate any 1849\AA light which was found to photolyze the solvents. Occasionally, concentrations of 10^{-4}M were used for analytical purposes.

After irradiation, normally for 15 minutes, the spectrum of the solution was obtained with the Beckman DK-2 spectrophotometer. The cell was again placed before the Hg lamp, and the process was continued for 3 more time intervals. The spectra of the irradiated solutions were compared with the spectrum of the unirradiated solution to determine what changes had occurred.

The number of quanta absorbed was determined by using a potassium ferrioxalate actinometer according to the method of Hatchard and Parker (Ref 22). The number of quanta absorbed by the solutions per minute was on the order of 10^{17} .

The disappearance quantum yields were calculated from the number of molecules decomposed per minute and the absorbed intensity.

Experiments were performed both in the presence and in the absence of oxygen. The latter condition was achieved by employing a Teflon stopper having two holes into which stainless steel tubing 0.032 inch in diameter was fitted. One tube was a vent while nitrogen was bubbled through a small flask containing solvent and then into the solution using the other tube. The tubes could be closed-off by slipping on small plastic tubing. It was found that five

minutes of rapid N₂ - bubbling was sufficient to remove the dissolved oxygen, since longer purges gave no difference in results. The replacement of the oxygen by nitrogen in the solution caused increased transmission at about 250 nm and below, which was taken into account in the analysis of the results.

RESULTS AND DISCUSSION

Ultraviolet Absorption Spectra of TNT and Other Aromatic Nitrocompounds

The spectrum of TNT in a nonpolar solvent could not be found in the literature. Therefore, the ultraviolet spectrum in cyclohexane will be presented and its discussion will also serve as a general example for all the aromatic nitrocompounds considered.

Figure 3 depicts the spectrum of TNT in cyclohexane with cyclohexane as the reference.

The shoulder at about 315 nm probably belongs to a class of transitions in which an electron is promoted from a nonbonding (n) molecular orbital in the ground state to an antibonding π (π^*) molecular orbital in the excited state. Therefore, this type is called an $n \rightarrow \pi^*$ transition. This transition occurs at a longer wavelength and has a much lower extinction coefficient than the highly intense $\pi \rightarrow \pi^*$ transitions in which an electron is promoted from a bonding π - orbital to an antibonding π -orbital. For TNT, the $n \rightarrow \pi^*$ band has an extinction coefficient of about 650 liter mole⁻¹ cm⁻¹ while, for the $\pi \rightarrow \pi^*$ transition at 224.5 nm, $\epsilon = 23,000$. The latter is to be compared with the work of Kamlet, Hoffsommer, and Adolph (Ref 23) who obtained $\epsilon = 19,200$ at $\lambda_{\text{max}} = 227$ nm for TNT in methanol. The bathochromic shift in going from nonpolar to polar solvents is characteristic of $\pi \rightarrow \pi^*$ transitions. As is shown below, this is also true for nitrobenzene in n-heptane and isopropyl alcohol. The shoulders at about 300 and 290 nm, with extinction coefficients of about 1000 and 1200 respectively, probably also belong to the same or different $\pi \rightarrow \pi^*$ transitions, since the extinction coefficients are somewhat larger than those expected for $n \rightarrow \pi^*$ transitions.

The spectra of other aromatic nitrocompounds, mostly in n-heptane, were studied to determine how the number and position of methyl and nitro-groups affect the spectral behavior of this class of compounds. The wavelengths and extinction coefficients of the main ($\pi \rightarrow \pi^*$) absorption band for each are given in Table 3.

TABLE 3

Wavelengths and extinction coefficients of the main ($\pi \rightarrow \pi^*$) absorption bands of some aromatic nitro-compounds in region $\lambda > 220$ nm

The solvent is n-heptane unless otherwise indicated

<u>Aromatic Nitrocompound</u>	<u>λ_{max}, nm</u>	<u>ϵ_{max}, liter mole⁻¹ cm⁻¹</u>
Nitrobenzene	252	8810
Nitrobenzene (isopropyl alcohol)	258	8500
o-Nitrotoluene	251	5890
m-Nitrotoluene	256.5	8190
p-Nitrotoluene	264	10100
m-Dinitrobenzene	228	18800
2,4-Dinitrotoluene	233	15800
TNT (Cyclohexane)	224.5	23000

The results are in good agreement with values found in the literature.

It can be seen that the introduction of the second nitrogroup causes λ_{\max} to decrease and ϵ_{\max} to increase. The third nitrogroup does not appear to be of great significance in this connection. Not shown here are indications of highly absorbing bands at wavelengths below 220 nm.

Spectra and Mean Lifetimes of Intermediates Produced by Flash Photolysis

The results obtained in this work are consistent with the observations of Margerum et al (Ref 6) in that only those compounds which have a nitrogroup ortho to a benzyl hydrogen yield an intermediate which absorbs in the visible region of the spectrum, that is, only for o-nitrotoluene, 2,4-dinitrotoluene, and TNT were intermediates observed. It was also found that the spectral characteristics and mean lifetimes of the intermediates in nonpolar solvents were independent of the presence of oxygen, at least for o-nitrotoluene and TNT which were checked (2,4-dinitrotoluene was done only in the presence of air). The mean lifetime of an intermediate is determined from the oscilloscope trace as follows:

Since it was found that intermediate decay obeyed first order kinetics, one can write

$$C = C_0 e^{-kt} \quad (1)$$

where C is the concentration of the intermediate at time t, C_0 is the concentration at zero time and k is the rate constant. Taking common logarithms:

$$\log C = \log C_0 - kt (0.4343) \quad (2)$$

Now, from Beer's law: $I = I_0 (10)^{-\epsilon Cl}$ (3)

where I_0 is the initial intensity and I is the intensity after transmission through a path length of l and a solution of concentration C having an extinction coefficient ϵ at a particular wavelength. Taking common logarithms of Equation (3) and rearranging the terms gives

$$C = \frac{-\log \left(\frac{I}{I_0} \right)}{\epsilon l} \quad (4)$$

Now, taking logarithms of Equation (4),

$$\log C = \log \left[-\log \left(\frac{I}{I_0} \right) \right] - \log \epsilon l \quad (5)$$

Combining Equation (5) with Equation (2) for time t and time zero leads to

$$\log \left[-\log \left(\frac{I}{I_0} \right)_t \right] = \log \left[-\log \left(\frac{I}{I_0} \right)_0 \right] - kt (0.4343) \quad (6)$$

In Equation (6), $\left(\frac{I}{I_0} \right)_t$ and $\left(\frac{I}{I_0} \right)_0$ are the transmissions at time t and at time zero, respectively. A plot of $\log \left[-\log \left(\frac{I}{I_0} \right)_t \right]$ vs t gives a straight line with

$$k = -\frac{\text{slope}}{0.4343} \quad (7)$$

so that

$$\tau_m = \frac{1}{k} = -\frac{0.4343}{\text{slope}} \quad (8)$$

where τ_m is the mean lifetime.

Unfortunately, as is indicated earlier in this report, I_0 does not remain constant, the reason being the formation of a product or products that absorb in the same wavelength region. This type of behavior has also been observed by Wettermark (Ref 8, 9). Therefore, I_0 was taken as that value for the transmission after the decay of the intermediate. Only the first few flashes were given consideration since the I_0 decreased rapidly thereafter. The result of this behavior was a loss of accuracy in determining the mean lifetimes, especially when the intermediate absorption was small. The wavelength of maximum absorption (minimum transmission) for the TNT intermediate appears to be in the 470 nm region. The mean lifetime is determined to be 1.5 ± 0.3 msec.

The experimental transmissions and wavelengths observed for the TNT intermediate are given in Table 4.

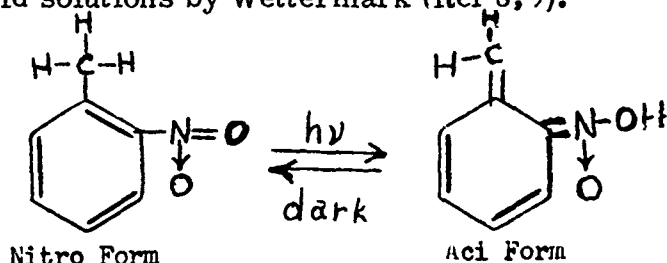
TABLE 4

Spectral data for the TNT intermediate produced by flash photolysis*

τ_{nm}	% Transmission
400	92.6
450	80.8
500	81.7
550	93.6

*A more complete spectrum for this intermediate, obtained by C. Capellos and R. Suryanarayanan, will be published soon.

The spectra of the intermediates of o-nitrotoluene ($\lambda_{max} \sim 370$ nm) and 2,4 dinitrotoluene ($\lambda_{max} > 350$ nm) as well as the lifetime of the o-nitrotoluene intermediate were consistent with their being aci-forms of the nitrocompounds; such intermediates were observed in aqueous acid solutions by Wettermark (Ref 8, 9).



The TNT intermediate is also assumed to be a similar aci form by analogy with the above and the long lifetime which is characteristic of isomeric interconversions. Since the concentrations of the intermediates were not known, it was not possible to determine their extinction coefficients.

Quantum Yields for the Disappearance of Aromatic Nitrocompounds

The disappearance quantum yields determined for the continuous irradiation with 2537Å are given in Table 5.

TABLE 5

Disappearance quantum yields of aromatic nitrocompounds irradiated with 2537Å light

<u>Aromatic Nitrocompound</u>	<u>$\bar{\Phi} \times 10^3$</u>
Nitrobenzene	3
Nitrobenzene (isopropyl alcohol)	2
o-Nitrotoluene	4
m-Nitrotoluene	0.8
p-Nitrotoluene	2
m-Dinitrobenzene	1
2,4-Dinitrotoluene	1
TNT (Cyclohexane)	1

It was found that the quantum yields were independent of oxygen in the solutions, within an experimental error of ~20%. The quantum yields were also independent of the intensity within the range investigated: 9×10^{16} to 5×10^{17} quanta/minute.

The formation of products having absorption near the spectral peaks of the aromatic nitrocompounds, where the quantum yields were evaluated, causes the quantum yields to be minimum values. However, the values are not expected to be very far from the true values in view of the small dependence of the quantum yields on time of irradiation. This indicates that no significant product interference is occurring.

For comparison, nitrobenzene in isopropyl alcohol was also investigated. Anomalous results, apparently due to the photo-decomposition of the products, appeared within the 45-minute irradiation period. Therefore, 5-minute intervals of irradiation totaling 20 minutes were used.

As is stated in the Introduction, most of the previous attempts to study the products obtained from the photolyses of aromatic nitrocompounds were performed with continuous irradiation in the 365-366 nm region of the spectrum. Absorption in this region corresponds to the $n \rightarrow \pi^*$ transition, generally but not fully accepted (Ref 24). The lowest triplet state is considered a π, π^* state by Baltrop and Bunce (Ref 16), but Trotter and Testa (Ref 25) give evidence that this is incorrect and that the state is n, π^* . It has been reported that while most of the molecules apparently return by internal conversion to the ground state, some of the molecules undergo intersystem crossing to the triplet state which is the reacting species (Ref 13).

On the other hand, absorption at 2537\AA corresponds to the $\pi \rightarrow \pi^*$ transition. Since the main absorption bands of the aromatic nitrocompounds are in the 2537\AA region or somewhat lower, the essential effect of the flash photolysis is the excitation of the same $\pi \rightarrow \pi^*$ transition. Therefore, it should be expected that the primary processes in flash photolysis and in our continuous photolysis should be the same.

When the flashed solutions were held in the dark overnight and their differential spectra observed again, it was found that the overall transmissions increased somewhat but the shapes of the curves were essentially the same as before. With the continuous irradiated solutions, this generally did not occur to any significant extent.

A comparison of the quantum yields for the disappearance of the aromatic nitrocompounds reveals that the values are small and essentially not too different (see Table 5). This indicates that the most important reaction (or reactions) occurring is the deactivation to the ground state of the original molecule as exemplified by Reaction (5) depicted in Table 1. Since these aromatic nitrocompounds do not usually fluoresce, the deactivation must take place by some other means (Ref 13, 24).

Product Formation

As might be expected, some product bands were more prominent with some of the nitrocompounds than with others. Since, in many cases, the reference solutions used in the spectrophotometric determinations were the original solutions, the differential curves were not quite true spectral representations of the products. This is due to the fact that the loss of aromatic nitrocompound due to photolysis is not completely compensated by the reference solution. However, any product or products that are formed having high extinction coefficients should be easily observed.

The changes in transmission of photolysis experiments for nitrobenzene in n-heptane, o-nitrotoluene in n-heptane, and TNT in cyclohexane are given in Figure 4. Decreases in the concentrations of the parent nitrocompounds are seen through increases in transmission at their respective absorption bands. Another feature of these curves is also quite obvious: there are two points for the nonnitrocompounds that do not change with irradiation time. These points are called isosbestic points (sometimes this term is applied only to equilibrium conditions and the term iso-absorptive points to time-dependent reactions) (Ref 26). All the photolyses result in isosbestic points and, in the flash photolysis work, each of the final flashed solutions crossed the original solution curves at these same points. The polynitrocompounds showed only one isosbestic point since the main absorption bands were at the extremes of the curves and were not explored to lower wavelengths. Table 6 compares the isosbestic points for nitrobenzene, o-nitrotoluene, and TNT.

As examples of the differential spectrophotometric curves, those obtained with nitrobenzene in n-heptane, with o-nitrotoluene in n-heptane, and with TNT in cyclohexane are given in Figure 5. The differential bands for the three aromatic nitrocompounds are compared in Table 6. For TNT, the lower wavelengths could not be investigated because of the overpowering absorption by the TNT itself. Except for different transmission values due to different amounts of conversion, the curves for the continuously photolyzed nitrocompounds were identical to the curves obtained by flashing.

TABLE 6

Isosbestic points and differential spectral bands
of nitrobenzene, o-nitrotoluene, and TNT

<u>Compounds</u>	<u>λ (nm), isosbestic points</u>	<u>λ (nm),</u>
		<u>Differential Spectral</u> <u>Band</u>
Nitrobenzene in n-heptane	226	219
	274	286
		283
		292
		302
o-Nitrotoluene in n-heptane	235	225
	269	280
		285 (Shoulder)
		316
TNT in cyclohexane	262	274
		295 (Shoulder)
		310

The differential uv spectral characteristics of the products formed in all the photolyses suggest the possibility of aromatic nitrosocompounds. This is particularly true for o-nitrotoluene (and possibly for TNT). Figure 6 is the ultraviolet spectrum of o-nitrosotoluene in n-heptane. The spectrum indicates shoulders at 310, 280, and 227 nm, as well-defined bands at 287.5 and 220 nm (also a further band at ~ 207.5 nm, which appeared to be somewhat more absorbing than that at 287.5 nm). The extinction coefficients were determined to be ~ 9100 at 287.5 nm and ~ 4310 at 310 nm. Also, o-nitrosotoluene has a very weak band at 790 nm with an observed extinction coefficient of 39.6 due to the nitroso group.

To check on the identity of the product as o-nitrosotoluene in the photolysis of o-nitrotoluene, the amount of o-nitrotoluene lost through photolysis was calculated and a synthetic solution was prepared, consisting of the o-nitrotoluene remaining and an equivalent amount of o-nitrosotoluene corresponding to the lost o-nitrotoluene. The differential curve is given in Figure 7. It can be seen that the overall features are those found in the photolyzed solution depicted in Figure 5b. The band at 225 nm has a transmission greater than 100%, indicating at least one other product must be present.

To further substantiate the presence of o-nitrosotoluene, a 10^{-4} M o-nitrotoluene solution was flashed fifteen times and concentrated under vacuum. A similar solution of nitrobenzene was treated in the same manner. The concentrated o-nitrotoluene solution showed a very weak, but definite band at 790 nm. On the other hand, the concentrated nitrobenzene solution showed no band in the 700-800 nm region. Even when flashed 30 times the nitrobenzene solution did not give any definite indication of a band in this region.

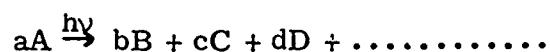
In addition to the ultraviolet region, the visible region between 340-900 nm was also observed for the photolyzed aromatic nitro-compounds. For nitrobenzene and p-nitrotoluene, the differential curves (90-100% transmission range) indicated for each a weak band in the 350 nm region. With the other nitrocompounds, this band was either absent or indefinite.

The 350 nm band observed in the photolyzed solutions of nitrobenzene suggests a nitrophenol. This was tested by continuously photolyzing a 10^{-4} M nitrobenzene solution for 5 hours at 2537Å (essentially equivalent in percent decomposition to one hour with a 10^{-5} M solution). The solution was extracted with aqueous 0.01N NaOH, in which the spectra of the nitrophenols have been studied by Kiss and Howath (Ref 27). Bands at 405, 282, and 230 nm were observed in the extracted aqueous phase. These bands are to be compared with the literature values of 415, 282, and 225.5 nm for o-nitrophenol.

In the case of the photolyzed o-nitrotoluene, no such bands were observed except by extracting the o-nitrotoluene solution that was flashed fifteen times and concentrated under vacuum. Here a weak, broad band in the 405-410 nm region was obtained. The lack of spectral data for possible nitrophenols prevents an assignment at this time.

The above results suggest that, in the photolysis of o-nitrotoluene, the main product is o-nitrosotoluene and the secondary product is a nitrophenol. In the case of nitrobenzene, the main product appears to be o-nitrophenol. Thus, an intramolecular process may be occurring to some extent. If nitrobenzene lost an oxygen atom as a result of the absorption of a photon, nitrosobenzene would be expected as a product. For the present conditions, a positive indication of nitrosobenzene would be absorption at 760 nm. However, the absorption here is weak, and therefore only possible for large amounts of nitrosobenzene. Nitrosobenzene has been suggested as an intermediate product even though it has not been observed (Ref 16). Its failure to appear is attributed to secondary photolysis and chemical reactions. Similarities in the differential spectra suggest that aromatic nitrosocompounds and nitrophenols are also products in the photolyses of the other aromatic nitrocompounds.

Any products produced must conform to the constraints of the isosbestic points. The conditions imposed in a photolytic reaction,



where a moles of original material A is photolyzed to products b moles of B, c moles of C, d moles of D, and so on, is that at each isosbestic point the relationship among the extinction coefficients be as follows:

$$\epsilon_A = \frac{b\epsilon_B + c\epsilon_C + d\epsilon_D + \dots}{a}$$

Attempts were made to fit solutions containing o-nitrophenol and/or nitrosobenzene to the isosbestic points observed in the photolyses of nitrobenzene. These mixtures could not be fitted to the observed isosbestic points in a simple manner.

The extraction experiments have also indicated other products present, some of which may have low extinction coefficients in the spectral range studied. The latter may be necessary to accommodate the isosbestic points.

With regards to products, the role of oxygen is not clear at this time. The differential curve of flashed TNT, depicted in Figure 5c was obtained with oxygen present. When oxygen was removed, the curve in the region of the 310 nm band had substantially smaller transmission values (greater absorption). Although the curve now had been altered at the higher wavelengths, the general shape was essentially the same and no other bands were obvious. However, in the case of o-nitrotoluene in n-heptane, only a slight change was noted at 340 nm.

CONCLUSIONS

Apparently, the processes are more complex than had been indicated by a superficial observation of the data. That the photochemistry of the aromatic nitrocompounds is quite complex is shown by the review of the literature given in Table 2. Specifically, it is shown by the fact that free radicals have been observed by means of electron spin resonance in the photolysis of o-nitrobenzaldehyde, o-nitrocinnamic acid and o-nitrobenzyl alcohol, while negative results were obtained with nitrobenzene and o-nitrobenzoic acid (Ref 10). It was also observed that the free radicals produced by o-nitrobenzaldehyde was of such low concentration that it is not expected to be an intermediate in the photochemical rearrangement to a nitrosocompound. Free radical intermediates were also observed for o-nitrocumene, o-nitroethylbenzene and o-nitrotoluene (in the last case, a very small amount)(Ref 15) by ESR. These radicals were stable for days and could be produced in the presence or absence of oxygen. Irradiation of the corresponding parasubstituted compounds gave no radicals. No evidence for the presence of radicals has been obtained in the visible region.

As is stated in Section B, the intermediates observed by the visible spectra of the flashed aromatic o-nitrocompounds are consistent with the aci form of the compounds. The relatively long lifetimes of the intermediates show that they are not excited singlet states. In addition, it is also unlikely that triplet states are involved since the same results were obtained in both the presence and the absence of oxygen, unless the triplet lifetime is less than approximately 20 μ sec - the experimental limitation.* It is known that oxygen is an excellent quencher of triplet states.

It appears that the aci and radical intermediates observed are due to side reactions and are not related directly to the products. (Ref 8 and 10) In addition, the lack of a significant oxygen effect on the quantum yields and products indicates that the intermediates are not long-lived triplet states. Even at the longer wavelengths, the triplet state is not involved in the photolysis of nitrosobenzene, and in the photolysis of nitrobenzene participation of the triplet state has not been established unequivocally (Ref 19). Apparently, the intermediates responsible for the products have not been observed as yet.

The results of this study indicate that further progress in elucidating the detailed mechanisms involved in the photolyses of aromatic nitrocompounds requires the extensive development of analytical techniques to determine quantitatively the products obtained. This study and the previous literature imply that this is not an easy task.

*Capellos and Suryanarayanan have recently shown, in low temperature flash photolysis studies conducted in a PMMA matrix, that the triplet state for trinitrobenzene is not expected to be observed at room temperature for the time resolution of the flash photolysis equipment used in this work. The reports listed below contains details of this work.

1. C. Capellos "Ruby Laser Nanosecond Flash Photolysis of α -Nitronaphthalene Solutions" Picatinny Arsenal Technical Report 4341, June 1972.
2. C. Capellos and K. Suryanarayanan "Microsecond Flash Photolysis of 1, 3, 5-Trinitrobenzene Solutions and Product Formation with 254 nm Steady State Illumination", Picatinny Arsenal Technical Report 4342, June 1972.

Further efforts will be concerned with the development of analytical techniques, which will include IR and UV spectroscopy, and thin-layer and gas-liquid chromatography. Furthermore, these analytical techniques will be applicable to shock decomposition studies of explosives containing aromatic nitrogroups which are in progress. Here the attempt is to detect chemical changes as a result of shockwaves passing through the explosive.

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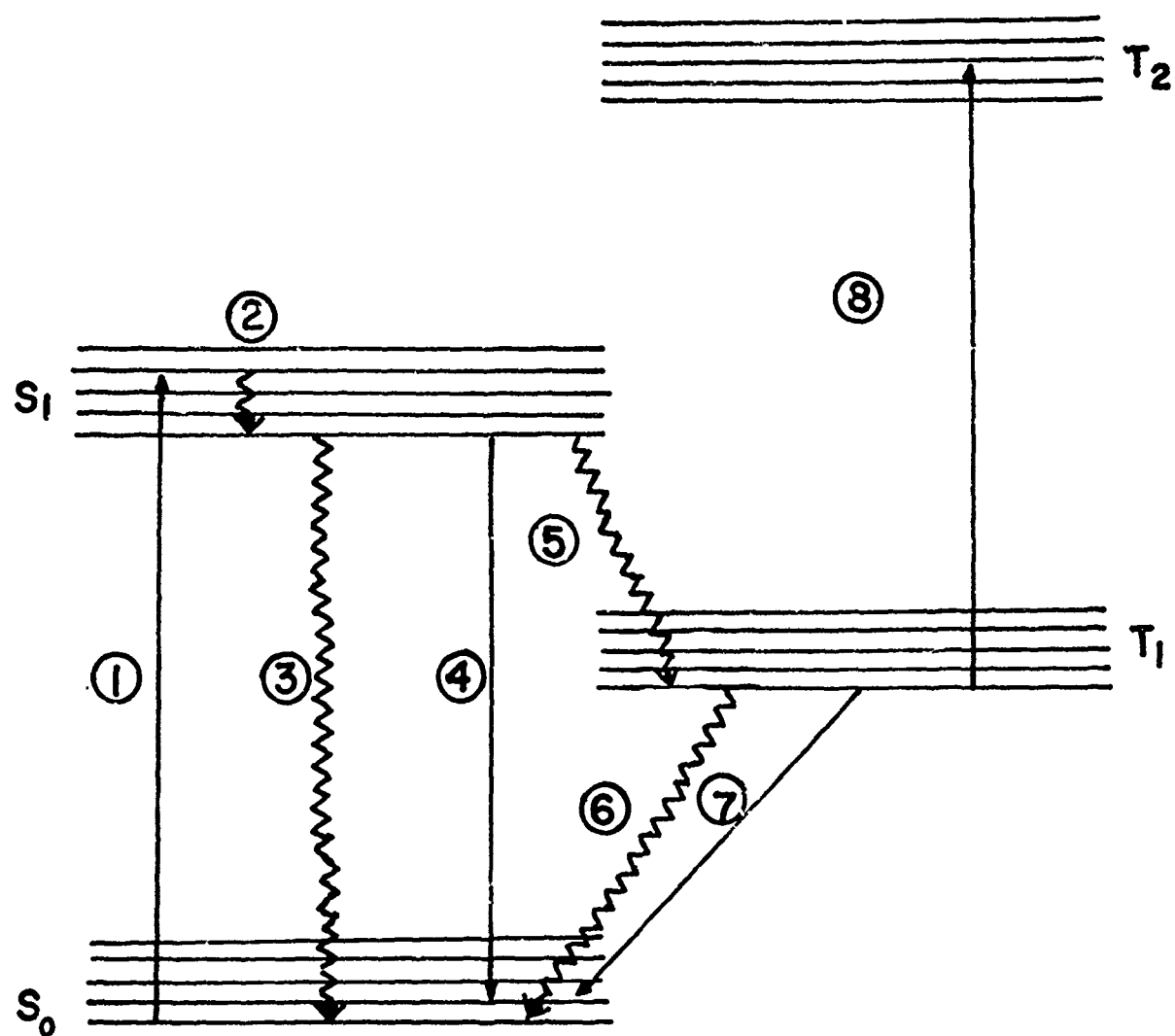


FIGURE I. SCHEMATIC REPRESENTATION of the ENERGY LEVELS of an ORGANIC MOLECULE CONTAINING a π -ELECTRON SYSTEM

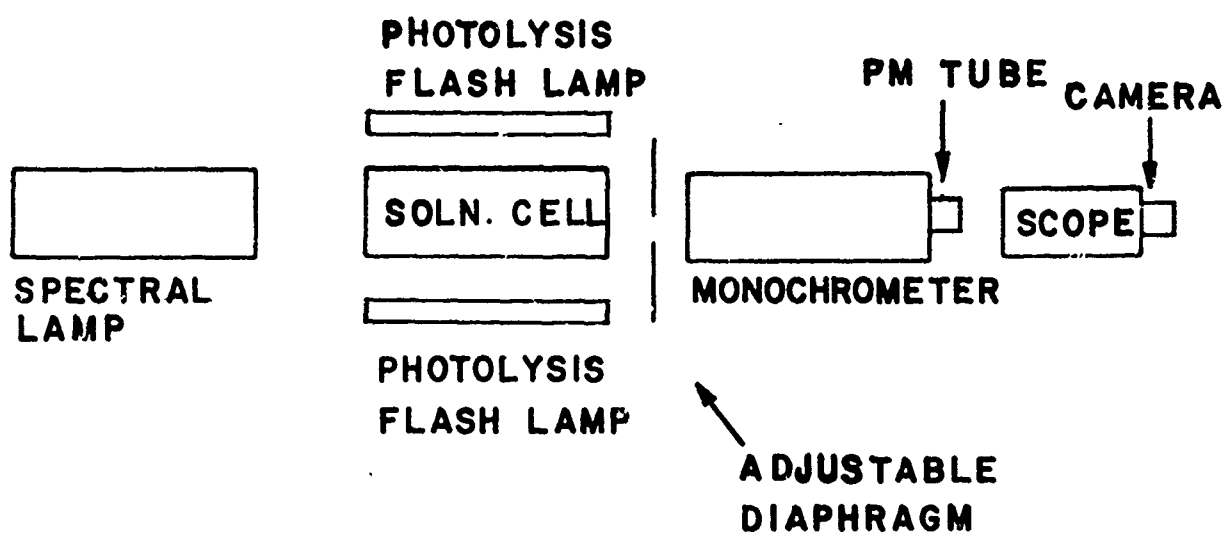


FIGURE 2. SCHEMATIC DIAGRAM of FLASH PHOTOLYSIS APPARATUS

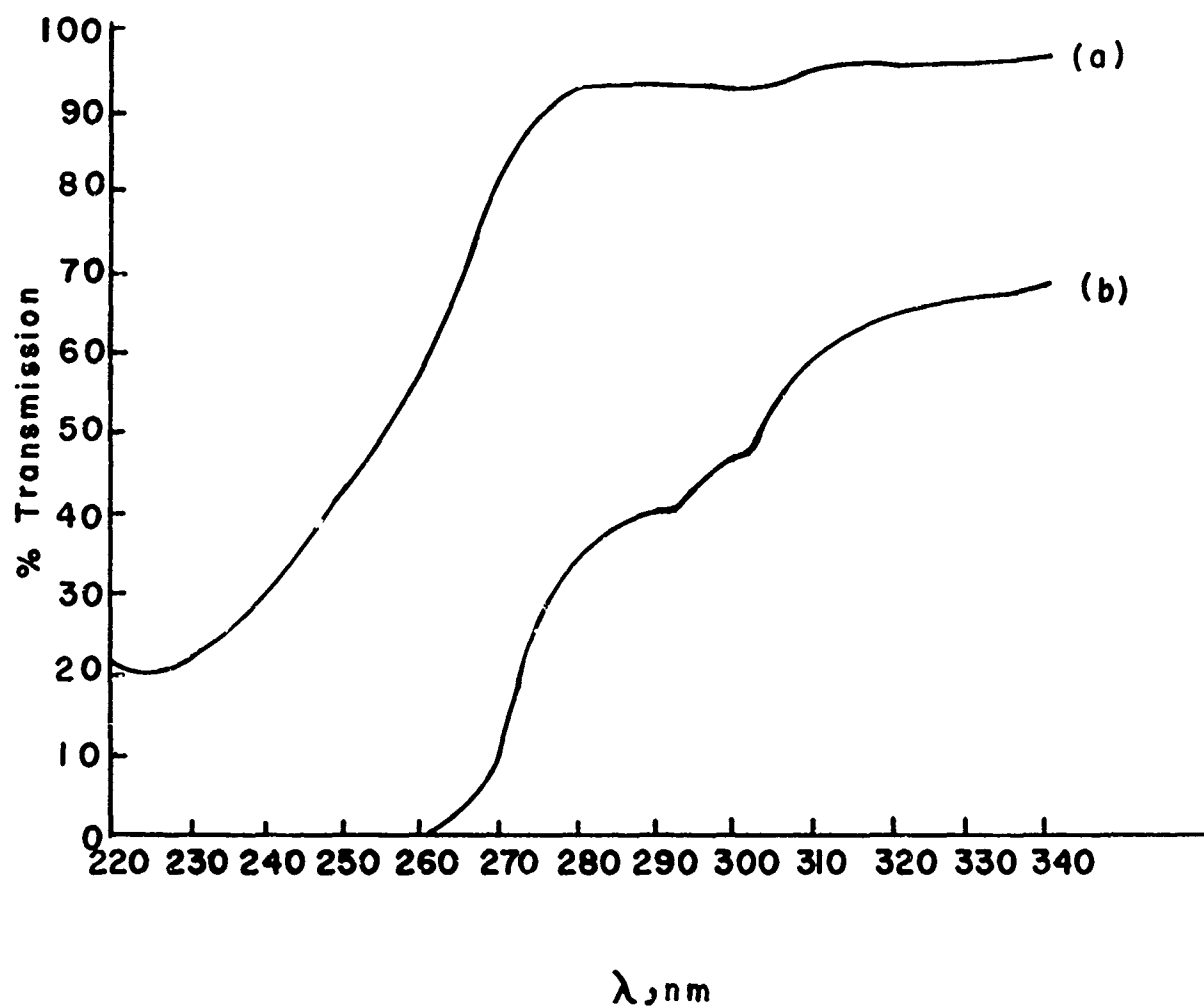


FIG. 3 Spectrum of TNT in Cyclohexane

(a) 3×10^{-5} M

(b) 3×10^{-4} M

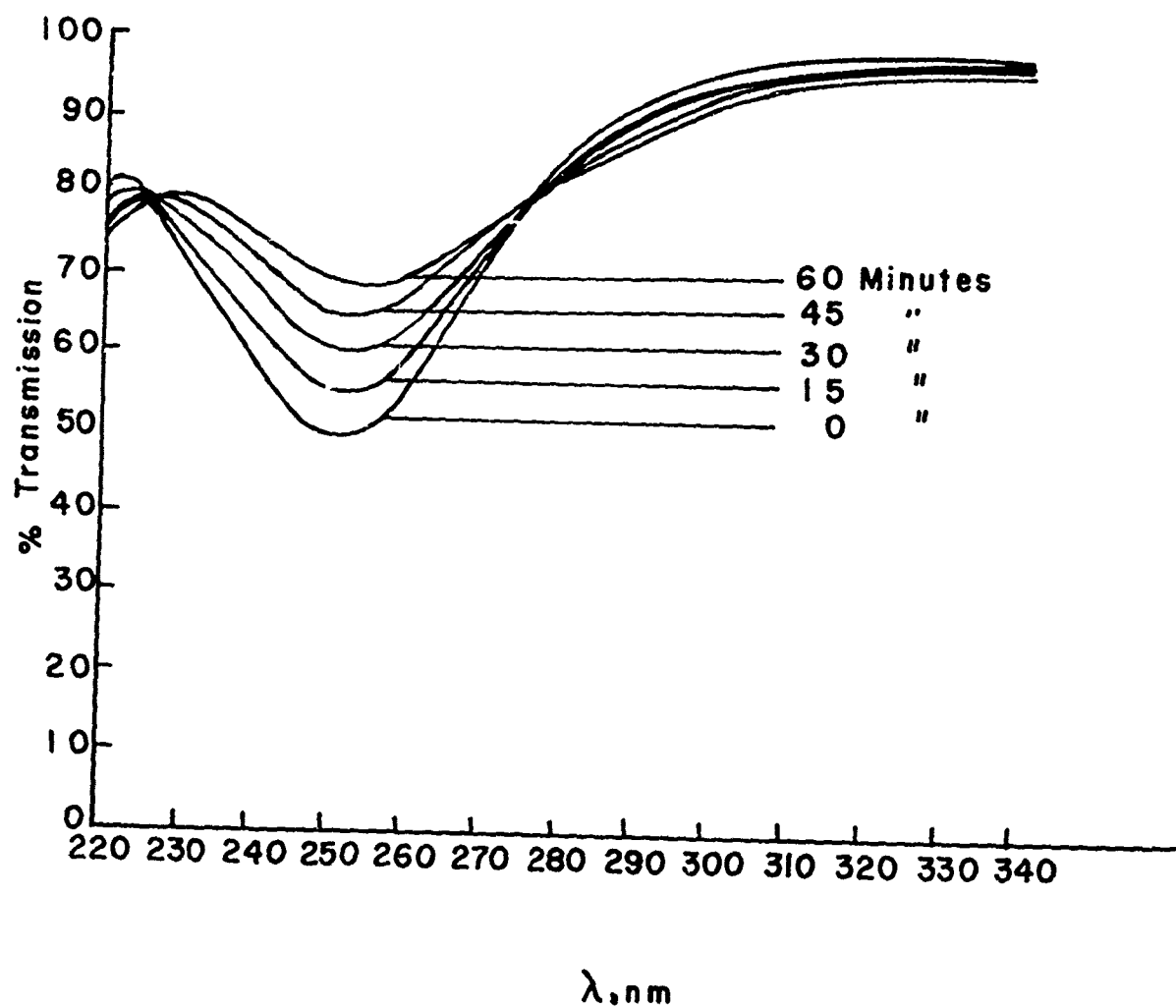


FIG. 4 Changes in Transmissions of Aromatic Nitrocompounds During Continuous Photolysis for One Hour at 15 Minute Intervals.

(a) 3.5×10^{-5} M Nitrobenzene in n-Heptane

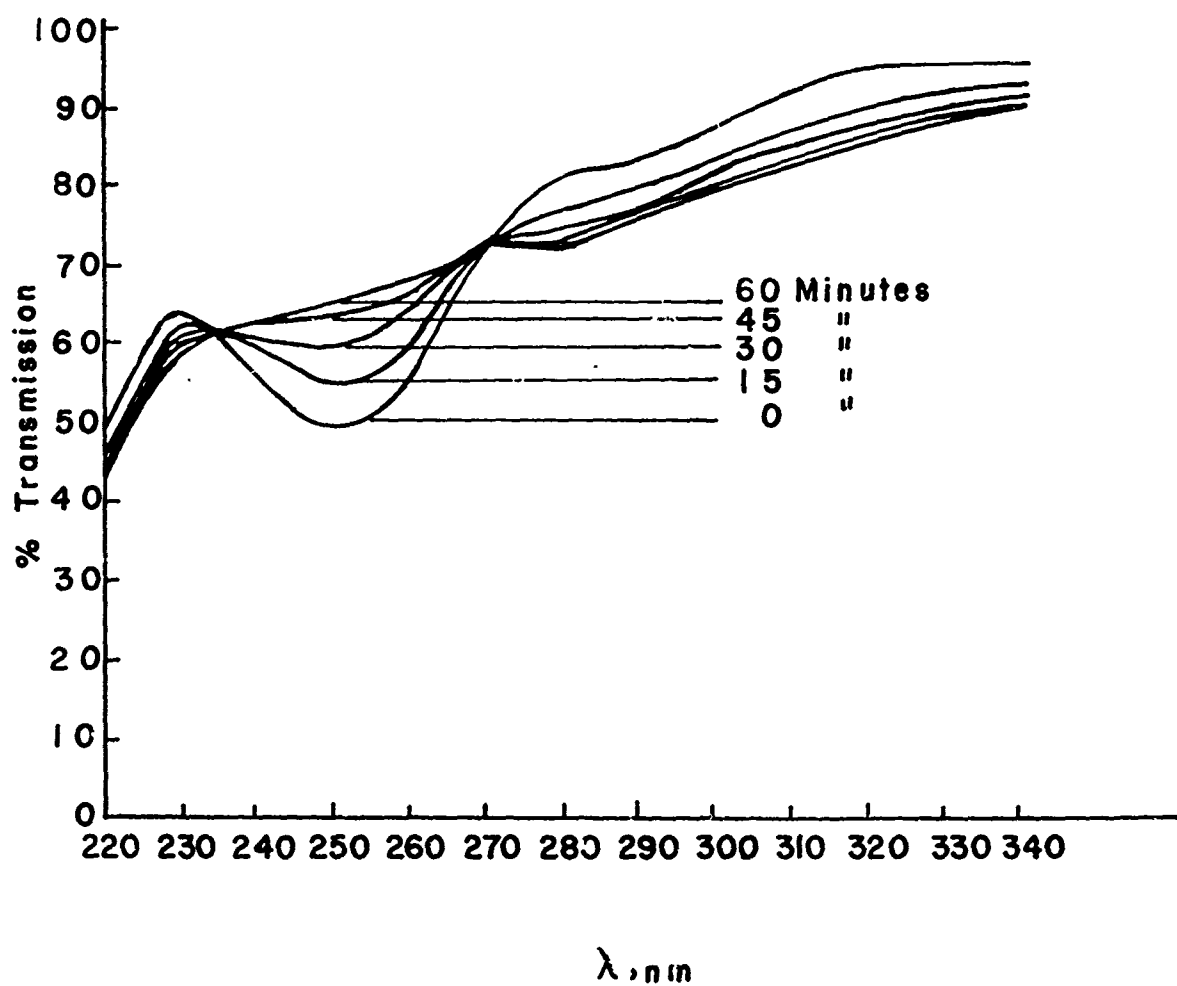


FIG. 4 Changes in Transmissions of Aromatic Nitrocompounds During Continuous Photolysis for One Hour at 15 Minute Intervals.

(b) $5.2 \times 10^{-5} M$ o-Nitrotoluene in n-Heptane

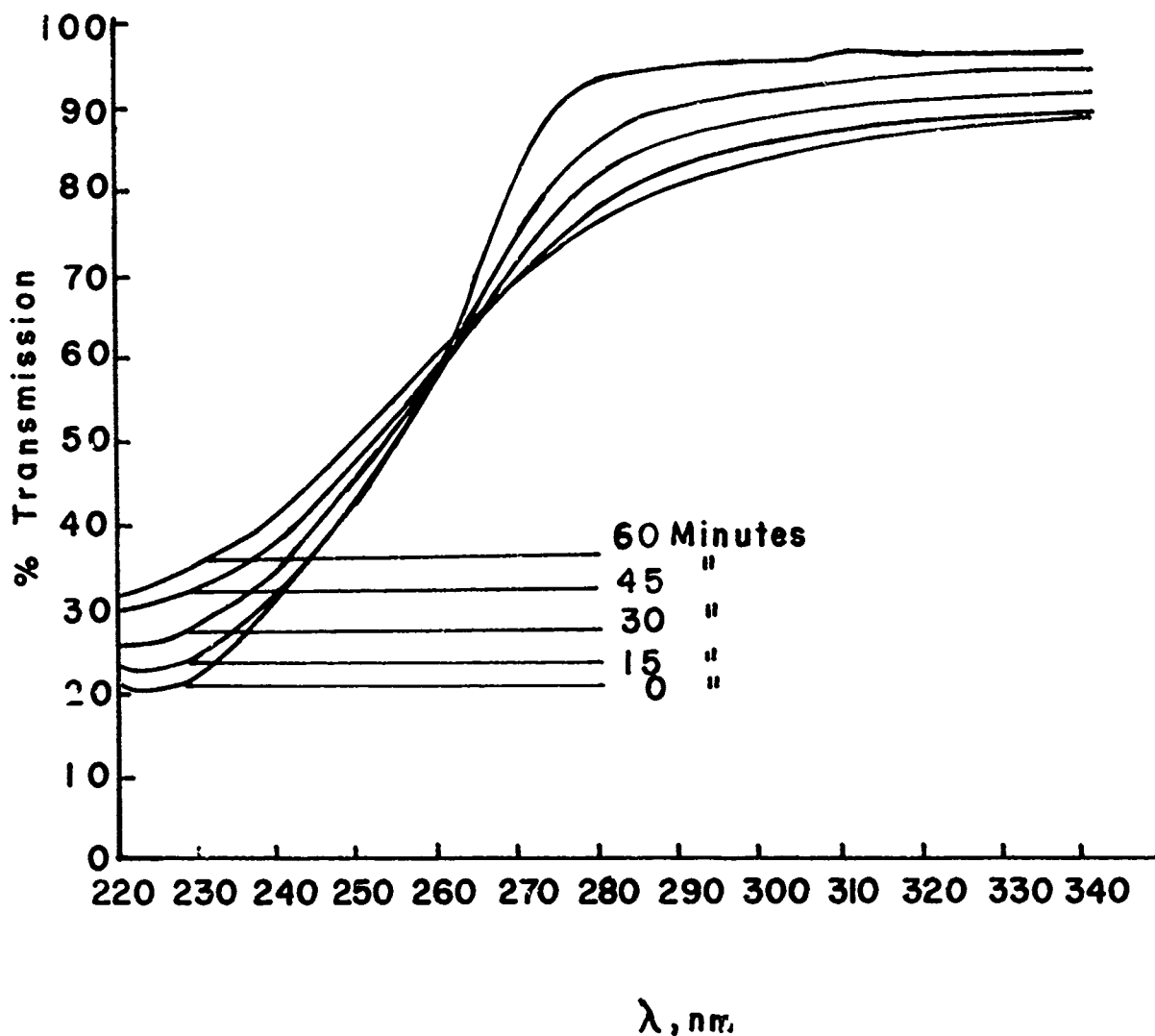


FIG. 4 Changes in Transmissions of Aromatic Nitrocompounds During Continuous Photolysis for One Hour at 15 Minute Intervals.

(c) 3.1×10^{-5} M TNT in Cyclohexane

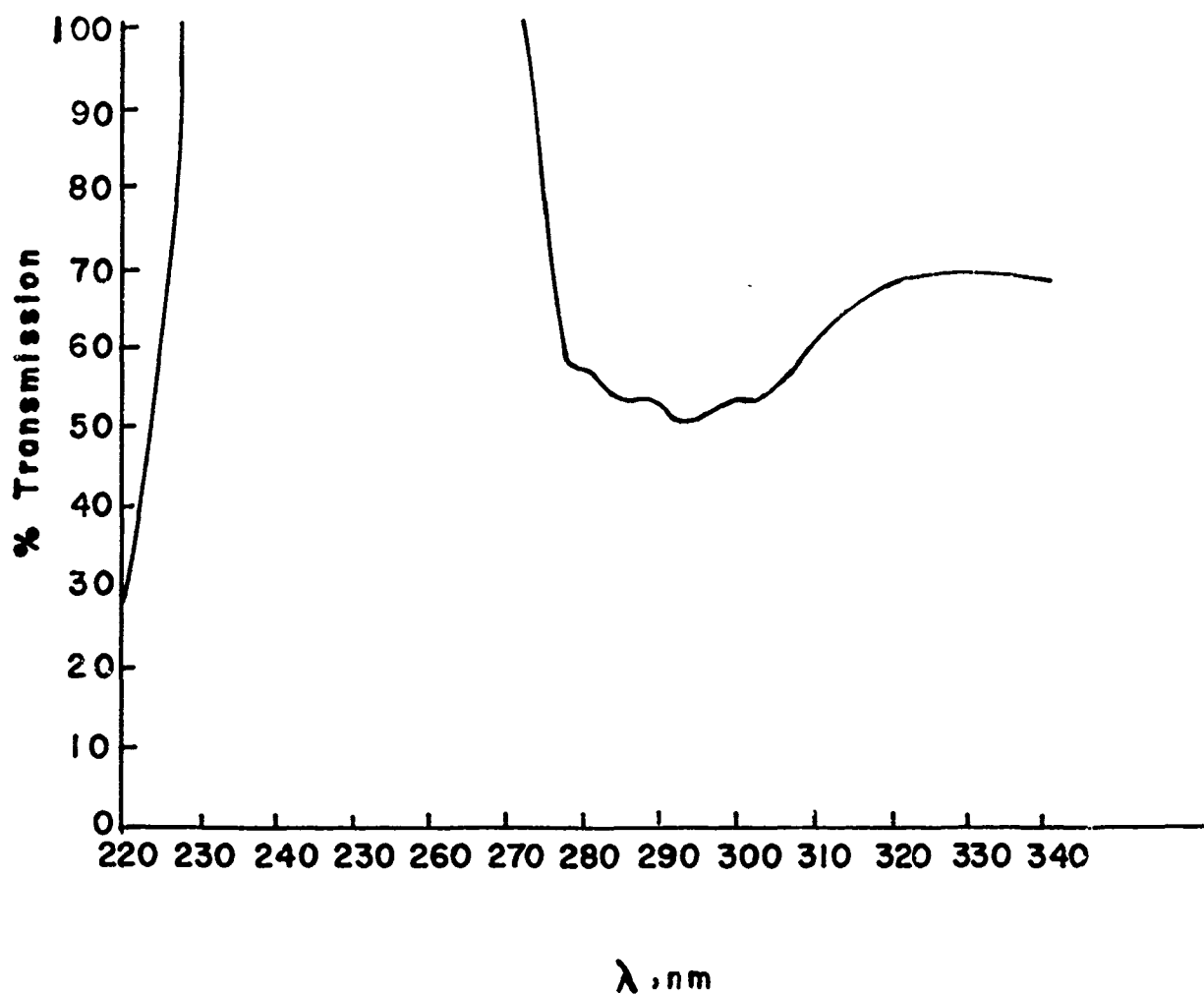


FIG. 5 Differential Spectra of Photolyzed Aromatic Nitrocompounds. References are unphotolyzed Solutions.

(a) 3.5×10^{-4} M Nitrobenzene in n-Heptane Continuously Photolyzed for 5 Hours.

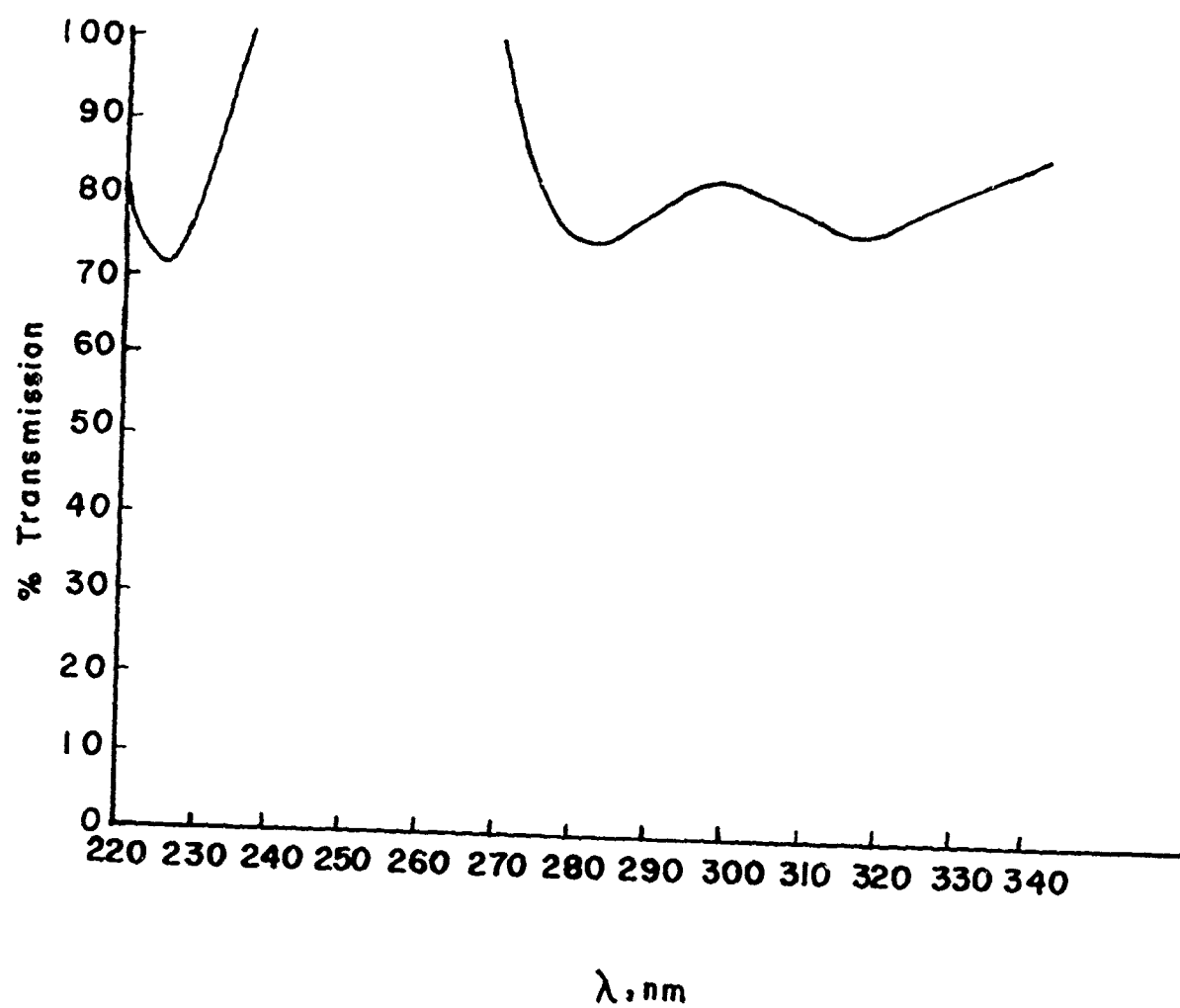


FIG. 5 Differential Spectra of Photolyzed Aromatic Nitrocompounds. References are Unphotolyzed Solutions.

(b) 2×10^{-4} M o-Nitrotoluene in n-Heptane
Photolyzed by Flashing 15 Times.